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Design of Mesomorphic Diarylethene-Based Photochromes

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The structural requirements for bistable photochromic (PC) systems, of which diarylethene derivatives are excellent examples,[1] and that for liquid crystal (LC) phase behavior in molecular systems seem so far to be almost noncompatible.[2] Diarylethene-based systems require alkyl or perfluorinated groups placed at strategic positions in the molecules to enable reversibility of the switching and to prevent degradation; thermotropic calamitic LC phase formation is in most cases associated with molecules with an overall cylinder shape. So far, bistable photochromic LCs have been obtained only by the connection of photochromic groups and mesogens by alkyl spacers in a modular concept or in dendrimers.[3]

The combination of photochromic and mesomorphic functionalities in a single center has, however, intrinsic advantages, as it has the potential to be synthetically much more efficient than the modular approach. Compared to modular LC photochromes, the volume density of switchable groups in the condensed phase (enhanced interactions in smectic layers[2a,c]) is increased, being comparable to that of azobenzene-based photochromes,[4] while exhibiting PC bistability and a high differentiation of the electronic properties (e.g., colorless−colored) of both forms.

To achieve this, the structural parameters determining the LC and the PC behavior have to be correlated to explore the functional scope of this approach. From an LC design point of view, diarylethenes can be viewed as dimers whose properties can be modulated by extending the length of the aromatic systems and/or terminal alkyl chains and by variation of the symmetry of the dimer. This is particularly effective where dipole groups are involved.[5] Melting behavior can be addressed by disrupting the packing of the aromatic groups; for that, fluorine groups are very suitable.[6] For photochromes the extension of the aromatic system should lead to bathochromic shifts of the absorption behavior. The variation in molecular symmetry is expected to have a strong effect too. The photoconversion processes, the extinction coefficients, and the fluorescence behavior should be modulated by this structural change as well. To investigate this, the symmetric "dimeric" systems **1** and **3** and the nonsymmetric molecule **2**, shown in Scheme 1, were prepared, all linked by a hexafluorocyclopentene group, ensuring the photochromic bistability of the systems.[1a,7] The final systems are based on the precursors **4** and **6**, which were obtained by two successive cross-coupling reactions. The preparation of the symmetric photochromes **1a** and **3a** was achieved by reacting the lithiated derivatives of **4** and **6** on a semi-equivalent of octafluorocyclopentene. The nucleophilic condensation of the lithiated derivative of **6** on **5** afforded the nonsymmetric photochrome **2a**.[8]

Table 1. Photochromic Properties of Compounds **1**, **2**, and **3**

	cyclization	cycloreversion	
compd	$\Phi_{a\to b}$ (λ_{irr})	conversion	$\Phi_{b\to a}$ (λ_{irr})
1	0.33 (313 nm)	>99	0.008 (546 nm)
2	0.13 (366 nm)	63	0.15 (546 nm)
3	0.006 (366 nm)	26	

The photochromic behavior of the systems **1**−**3** was investigated in cyclohexane solutions (2.05×10^{-5} mol L^{-1}). Figure 1a−c shows the absorption spectral changes of the systems under UV irradiation; 313 nm light was used for **1** and 366 nm light for **2** and **3**. The molecular variation of the systems altered significantly the absorption behavior of both forms. **1a** absorbs below 370 nm with an absorption maximum at 319 nm ($\epsilon = 7.8 \times 10^4$ mol^{-1} L cm^{-1}), while **3a** absorbs below 450 nm with an absorption maximum at 386 nm ($\epsilon = 5.4 \times 10^4$ mol^{-1} L cm^{-1}). For the 2-thienyl structure **3a**, the π-conjugation is extended over six aromatic groups, leading to a bathochromic shift of 65 nm when compared with the 3-thienyl structure **1a**, where the full π-conjugation is located only in each set of aromatic rings. An intermediate absorption behavior is observed for the hybrid structure **2a**; the foot band is located at 400 nm and the absorption maximum is centered at 321 nm ($\epsilon = 5.7 \times 10^4$ mol^{-1} L cm^{-1}). Irradiation of **1a**, **2a**, or **3a** with UV light resulted in solutions that were blue, red, or yellow, respectively. The formation of **1b**, **2b**, and **3b** is responsible for the change of the absorption behavior. Absorption spectra of the closed-ring isomers were calculated from the collected data.[3c,d] **1b** absorbs at 597 nm ($\epsilon = 2.7 \times 10^4$ mol^{-1} L cm^{-1}) as the π-conjugation is extended throughout the molecule. For **3b**, the formation of the C-sp^3 in the 3-position (at the thiophene group) disrupts the conjugation throughout the molecule, leading to an insignificant shift of the absorption bands (444 nm; $\epsilon = 8.5 \times 10^3$ mol^{-1} L cm^{-1}). The absorption behavior of the mixed system **2b** (518 nm; $\epsilon = 2.4 \times 10^4$ mol^{-1} L cm^{-1}) is between those of **1b** and **3b**. The position of the absorption bands of the open forms **1a**, **2a**, and **3a** and of the closed forms **1b**, **2b**, and **3b** can be viewed as a function of their π-conjugation lengths.[7] The photochromic properties are listed in Table 1. In this series, the quantum yields of photocoloration $\Phi_{a\to b}$ decrease with increasing π-conjugation of the open-ring isomers. The quantum yield of the cyclization reaction of **1a** was determined to be 0.33, while the yield of **2a** decreased to 0.13. For **3a**, $\Phi_{a\to b}$ was as low as 0.006. The same effect was observed for the quantum yields of the cycloreversion reaction $\Phi_{b\to a}$.[9] For **1b**, $\Phi_{b\to a}$ was very low, with a value of 0.008. For **2b**, $\Phi_{b\to a}$ increased strongly to 0.13. $\Phi_{b\to a}$ of **3b** could not be determined with our experimental setup[8] but is expected to be higher than the values of the other photochromes.[9b] The conversion value from the open form to the closed form at the photostationary state (PS), determined by HPLC,[8] was strongly dependent on the chemical structure of the photochromes. At 313 nm, the PS for **1** was reached in 1 min and the conversion from the open form **1a** to the closed form **1b** was almost 100%. The conversion value of **2** decreased to 63% and further to 26% for **3** (**2a**, **3a** irradiation at 366 nm). Only the 2-thienyl derivative **3a** exhibited fluorescence at 486 nm, with a fluorescence quantum yield of 0.021 (excitation at 366 nm). The fluorescence decreased only slightly over time as photoconversion from **3a** to **3b** is low, as shown in Figure 1d. The LC behavior of the open-ring isomers **1a**, **2a**, and **3a** was investigated using differential scanning calorimetry (DSC) and optical polarizing microscopy (OPM). The results are given in Table 2. The melting

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Scheme 1. Synthesis and Photochromic Interconversion of the Photoactive Mesogens

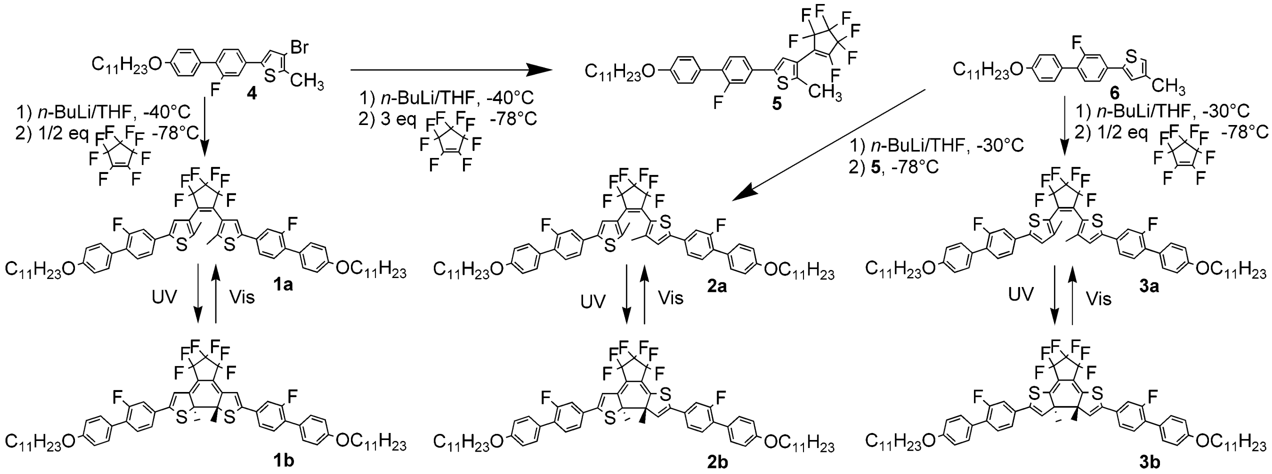

Table 2. Transition Temperature (°C) as Determined by DSC[a]

compd	transition temperature/°C (enthalpy, J g^{-1})				
1a[b]	Cr	99.8 (48.7)	N	84.2 (1.03)	Iso
2a[b]	Cr	91.6 (66.0)	N	29.8 (0.38)	Iso
3a	Cr	98.8 (69.2)	–		Iso
1b/1a (99/1)	Cr	95.5 (32.0)	N	74.1 (1.00)	Iso
2b/2a (63/27)	Cr	92.6 (68.9)	N	25.8 (0.27)	Iso
3b/3a (26/74)	Cr	91.0 (44.0)	–		Iso

[a] Cr = crystalline, N = nematic, Iso = isotropic. [b] Monotropic phase transition.

points are very low, considering that the systems consist of six aromatic rings. The symmetric structures **1a** (99.8 °C) and **3a** (98.8 °C) melt slightly higher than the nonsymmetric material **2a** (91.6 °C), likely due to a lower symmetry of this system. On cooling from the isotropic, the systems **1a** and **2a** exhibit a monotropic nematic phase at 84.2 and 29.8 °C, respectively, characterized by typical Schlieren texture. For the compositions at PS **1b/1a** and **2b/2a**, the nematic transitions are lowered to 74.1 and 25.8 °C, respectively. This reduction of the LC phase can be attributed to the reduction of flexibility of the central core; hence, the packing in the LC phase is less optimal. To the best of our knowledge, these are the first LC photochromic diarylethenes. The absence of LC behavior for **3a** and **3b/3a** at PS is, however, surprising. The reduction of the transition enthalpies (1.03 J g^{-1}) for **1a** and **1b/1a** (1.00 J g^{-1}), to (0.38 J g^{-1}) for **2a** and (0.27 J g^{-1}) for **2b/2a**, together with the values for the melting enthalpies (**3a** has by far the highest), suggests that the crystalline state for **3a** is strongly favored. The alignment of the dipoles in the most rigid part of the system in one direction could be responsible for that. Figure 1e,f shows an OPM sample of **1** heated above the clearing point and then quickly cooled to room temperature before and after irradiation (313 nm, 1 min).

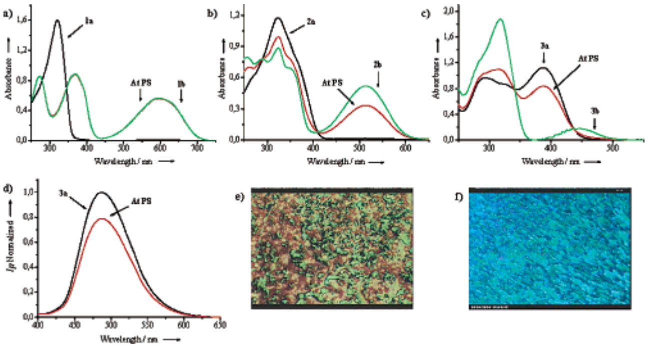

Figure 1. Absorption spectral changes of **1** (a), **2** (b), and **3** (c) and emission spectral changes of **3** (d) in cyclohexane solutions (2.05 × 10^{-5} mol L^{-1}). Polarizing optical micrograph of **1**, supercooled to room temperature, before irradiation (e) and after irradiation (f) of 1 min with 366 nm light.

It should be noted that the transition temperatures for systems irradiated in the condensed state or in solution are similar to those converted in solution and that for **1** PC behavior was observed in the crystalline state as well. In conclusion, we could show that it is possible to synthesize mesogenic diarylethenes without the linking to mesogens via alkyl spacers. Small variations in molecular structure affect the LC properties dramatically as well as the photoswitching, the absorption, and the fluorescence behavior of these systems.

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Supporting Information Available: Experimental procedures for the synthesis of the materials and the photochromic and fluorescence characterizations. This material is available free of charge via the Internet at http://pubs.acs.org.

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